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EASILY REMOVED CERAMIC RODS FOR CASTING GAS-TURBINE ENGINE BLADES USING MOLDING PATTERNS

A. V. Belyakov,[1, 3] I. V. Razumnova,[1] I. M. Demonis,[2] and Yu. I. Folomeikin[2]

Methods have been developed for weakening and removing ceramic rods from a metal casting by means of polymorphic transformations in cristobalite and β-Ca_2SiO_4 during vibration in water containing surfactants without the use of aggressive and environmentally harmful reagents. The hot-bending strength (at 1050°C) of ceramic made from cristobalite was about 20 MPa while that of β-Ca_2SiO_4 at 1300°C was 18 – 24 MPa, which is adequate for use as a rod material. The use of carbamide formaldehyde resin with silicate sol as a binder for powders made from tridimite, mullite and zircon made it possible to weaken the rods, on cooling, as a result of polymorphism of cristobalite. The weakening and removal of the rods during vibration in water containing a surfactant was achieved with a polymorphic transformation from β-Ca_2SiO_4 into γ-Ca_2SiO_4 in mixes made from MgO, α-Al_2O_3, fused SiO_2 and stabilized ZrO_2.

Key words: ceramics, casting using molding patterns, gas-turbine engine blades, weakening, polymorphism, cristobalite, dicalcium silicate.

VIAM and RKhTU collaborate in the most diverse fields of chemical technology. This concerns primarily technologies for producing and processing various types of materials (metallic, organic polymers, nonmetallic inorganic, composite) and their behavior while in use (interaction with the environment, protection from undesirable actions). The present article examines a quite narrow but important aspect of this collaboration – materials for ceramic rods used in casting blades from heat-resistant alloys for gas-turbine aircraft engines (GTE). As is well known, ceramic rods serve to form the inner cavity of the cooled GTE blades.

Casting using molding patterns is the principal industrial method of obtaining castings of blades with precise dimensions and quite high surface purity, so often the blades do not require further mechanical working [1]. The crux of the method lies in making a blade pattern from a material which can be removed (for example, on the basis of paraffin or urea). During fabrication a ceramic rod is placed in the pattern; the rod will form a cavity in the blade. Fine- and coarse-grain powders of refractory material (glassy SiO_2, α-Al_2O_3, $ZrSrO_4$, $Al_6Si_2O_{13}$ and others), which form a shell around the pattern, are deposited in layers on the pattern. To buildup strength each layer is allowed to harden before the next successive layer is added. Ordinarily, 2 – 12 layers are deposited, depending on the mass of the alloy poured on. Next, the patterns are removed (paraffin-based patterns are melted or burned out; urea-based models are dissolved in water). Patterns with ceramic rods present are heated through to remove any residues of organic substances and other gaseous precipitates and to buildup strength. Metal is poured into the heated patterns and crystallized to obtain blade castings with a prescribed structure. Often, the pouring is done in a vacuum or centrifugal force field [1]. The rods end up inside the cast blade. The rods must be removed in order for a blade-cooling cavity to form in their place.

The ceramic rods must satisfy requirements such as the following: smooth surface (height of the micro-asperities $Ra < 5$ μm); precision of the geometric dimensions — from $< \pm 0.15$ mm from nominal values; high bending strength (> 15 MPa); high porosity ($> 30\%$); and, stability against thermal shocks to temperature 1250 – 1300°C [1]. The rods must not deform when the metal is poured in. The deformation onset temperature under load 0.4 MPa must be $> 1450°C$ and conform to the conditions for pouring the metal. A rod is secured inside its cavity in a manner maintaining a small gap so that during heat-treatment the differences of the shrinkage and CLTE between the rod and the cavity do not engender thermomechanical stresses and

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[1] D. I. Mendeleev Russian Chemical Technology University (RKhTU), Moscow, Russia.
[2] Federal State Unitary Enterprise – All-Russia Scientific-Research Institute of Aviation Materials, National Science Center of the Russian Federation (FGUP VIAM), Moscow, Russia.
[3] E-mail: av_bel@bk.ru.

cracks in the rod. A rod must remain chemically stable when the melt is poured in; after cooling the rod must be completely removed from the casting. The dimensions of the cavity so formed must conform to the prescribed geometric values. The materials used for the ceramic rods should be inexpensive and readily available.

Rods can be sintered or cold-hardened (unsintered). Sintered rods are fired before they are placed into a pattern; cold-hardened rods are fired together only when the pattern is heat-treated. The grain compositions of the molding pastes for fabricating rods are chosen so that their shrinkage is small, not exceeding 1%. This creates the prerequisites for preserving the precision and reproducibility of rod dimensions.

The removal of rods from a blade casting is quite problematic. A chemical-hydraulic method has been developed at VIAM. This method combines the processing of the castings containing the rods in alkali solutions in an open bath or high-temperature autoclave and laving with a high-pressure stream of water.

In individual cases, melts of fluoride salts are used to remove corundum-based ceramic rods having a complicated shape. The drawback of this method was not so much the small corrosion of the blade metal as the ecological problems associated with the contamination of the environment with fluorine ions.

The department of the chemical technology of ceramics and refractories at the D. I. Mendeleev Russian Chemical Technology University together with its graduates working at VIAM has begun work on the development of easily removed rods for casting cooled blades from heat-resistant alloys.

First, Doctor of Technical Sciences E. S. Lukin and his colleagues worked on the fabrication of sintered MgO-based rods. Ceramic rods based on this material possessed adequate chemical inertness to a melt of VZhL-12U refractory alloy. The removal of such ceramic rods from blade castings was done in water under hydrothermal conditions. The rods were removed from regions where the thickest parts of the rods were located. No interaction with the inner surface of a casting was observed. In regions of thin sections of a rod (for example, in the zone of the blade body) the rod material became hydrated with $Mg(OH)_2$ being formed, which was accompanied by an increase of the blade volume. As a result, the rod was tightly pressed into the casting and could not be removed from it. In addition, in thin sections of the blade the expansion of $Mg(OH)_2$ sometimes caused the blade to deform.

Next, work was performed on the use of quartz for fabricating rods with polymorphic transformations occurring in cristobalite during cooling. The polymorphic transformations of cristobalite, accompanied by large volume changes, cause quartz-based ceramic rods to crack; this could make it easier to remove the rod from the metal casting of the blade after it has cooled.
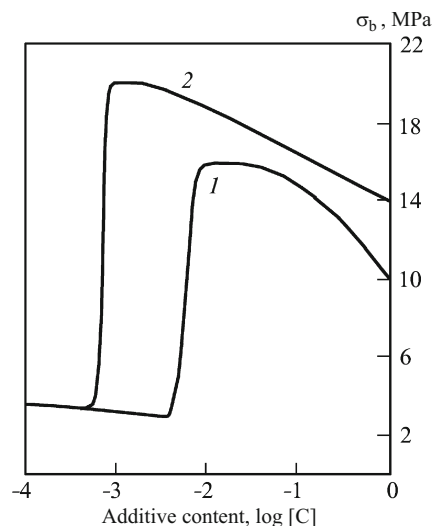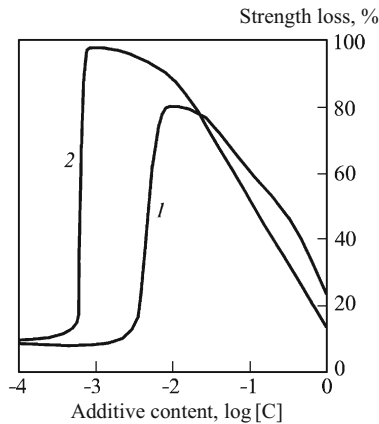

Fig. 1. Bending strength σ_b at 1050°C (after 5 h soaking at 1050°C) as a function of the additive content (C, wt.%): *1*) sodium oxide; *2*) potassium oxide.

A high-temperature polymorphic phase must be formed as the ceramic mold is heated before metal is poured in. A polymorphic transition occurs in the rod during subsequent cooling. This transition is accompanied by a change of volume. This caused the rod to fracture, which facilitates its removal from the casting. The use of the polymorphism of cristobalite results in an additional difficulty: during heat-treatment cristobalite starts to transform into tridimite and the loss-of-strength effect decreases or vanishes completely.

The samples were made using a binder consisting of carbamide formaldehyde resin (CFR). The grain composition of the molding pastes gave small shrinkage of the samples during drying and firing. There are many works devoted to the study of polymorphic transformations and the effect of additives during the heat treatment of quartz glass [2 – 4]. Pastes made from quartz glass with additives, alkaline oxides and alkaline-earth metals, promoting crystallization of the glass were used to realize a polymorphic transformation.

Additives degrade the high-temperature strength and resistance to the molten metal, so than their amounts must be minimized. Additions of NaCl and KCl were made during moistening of the powder by a water solution of the additive. The powder was dried, CFR was introduced, and the samples were molded. The samples were sintered for 5 h at 1050°C (the regime adopted at the plant) and the hot strength was determined at 1050°C (Fig. 1) and, after cooling, at room temperature. Heat-treatment transformed the glass into cristobalite with volume compression 0.9%. After cooling, volume reduction from 3.7 to 5.2% occurs at about 270°C as result of the polymorphic transformation α- $\rightarrow$ β-cristobalite, resulting in a loss of strength. The loss of strength, in percent, during cooling was determined for the ready samples (Fig. 2).

The added sodium oxide started to have an effect even at 0.001 wt.% in terms of Na_2O; the maximum bending

Fig. 2. Loss of bending strength after cooling from 1050°C to room temperature as a function of the additive content (C, wt.%): *1*) sodium oxide; *2*) potassium oxide.

TABLE 1. Variation of the Strength of Quartz Glass Samples Transformed into Cristobalite as a Function of the Na_2O/MgO Ratio in the Additive

Mass ratio Na_2O/MgO, %	Ultimate bending strength, MPa		Strength loss, %
	1050°C	20°C	
0.001/0.0001	20.5	8.7	96
0.001/0.001	21.8	4.1	98
0.001/0.01	20.3	0	100
0.001/0.1	17.3	0	100
0.001/1.0	14.7	0	100

TABLE 2. Variation of the Phase Composition of Silica Sol (Soaking at 1050°C)

Phase	Phase content, vol.%, after soaking, h				
	1	2	3	4	5
Glass	60	10	–	–	–
Cristobalite	40	90	60	50	45
Tridimite	–	–	40	50	55

strength obtained at 1050°C and the loss-of-strength (%) reached a maximum after cooling from 1050°C to room temperature. During the drying process the additive concentrated at the active points of the surface of the glass particles. Water is sorbed most strongly at these points and will evaporate last with the dissolved additive being concentrated in it. On heating a liquid phase forms at these points first, after which a cristobalite seed forms and then the entire grain crystallizes. For this, evidently, it is sufficient to have the liquid phase present at least at one point on the surface of a glass particle [5].

It is well known that additions of aluminum and boron cations impede the crystallization of glass [5]. These additives create oxide oxygen vacancies in silicon which retard diffusion mass transfer and the formation of cristobalite.

After the samples cooled, aside from sodium oxide, magnesium oxide was used to decrease their strength even more. The additions were introduced in the form of magnesium and sodium chlorides, which transformed into oxides during heat treatment. Sodium oxide was taken in the optimal amount 0.001 wt.% and a definite amount of magnesium oxide was added to it. The results are presented in Table 1. As evidenced in Table 1, the best results were obtained with Na_2O/MgO = 0.001/0.01. After cooling, the samples fell apart when touched.

When the soaking time was increased the cristobalite started to transform into tridimite and the loss-of-strength decreased. Thus, in samples with 0.001 wt.% Na_2O at 1050°C tridimite appeared after 5 h soaking (volume content 4%), and after 6 h soaking its volume content was about 20%.

The sintered-rod technology made it possible to overcome this difficulty. Quartz-glass blanks with no additives were formed using paraffin-pouring technology adopted at the plant and sintered. No transition into cristobalite was observed without additives being present. The bending strength of the blanks was 6 – 7 MPa; this corresponds to the commercial rods used and was adequate for transporting them

and checking their quality. A blank was permeated beforehand with oxalic acid, dried, and permeated with CFR to which a NaCl solution was added. The oxalic acid acted as a hardener for CFR. The NaCl additive became distributed uniformly in the blank. After permeation with resin the strength of the blanks increased to 10 – 12 MPa. On heating the resin burned up but the strength in the interval 300 – 600°C did not drop below 6 – 7 MPa, which is much higher than that of unsintered rods. When the molds were subsequently heat-treated before pouring the metal the quartz glass transformed into cristobalite, which fell apart when the casting cooled. The powder from the casting was removed by means of vibration in water using surfactants.

Quartz glass is quite expensive. For this reason, a decision was made to use other fillers and to obtain loss-of-strength by introducing a water silica sol into the CFR (CFR – silica sol). The composition with mass ratio CFR : silica sol = 1 : 1 (50 wt.% SiO_2 in silica sol) was adopted as optimal for obtaining the subsequent loss-of-strength. At temperature 1050°C the silica sol transformed quite sharply into cristobalite. The changes of the phase composition of silica sol after soaking at 1050°C are shown in Table 2. To obtain the maximum loss-of-strength after cooling the heat-treatment time of the blanks at 1050°C must not exceed 2 h, so as to avoid a transition of cristobalite into tridimite. The filler must not interact with highly disperse silicon oxide so as not to lose the loss-of-strength effect. Marshallite (finely disperse β-SiO_2), transformed into tridimite, and $ZrSiO_2$ and $Al_6Si_2O_{13}$ meet this requirement. Samples were made with these fillers based on the binder CFR – silica sol. The change of the hot strength of the samples during heat treatment is
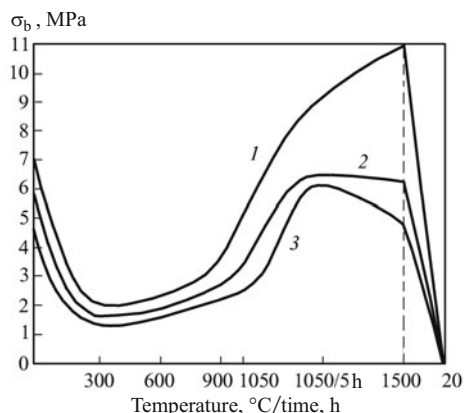
Fig. 3. Variation of the hot strength of the samples under bending σ_b as they are heated to 1050°C, after soaking at 1050°C for 5 h and after cooling to 20°C (content 30 vol.%; binder CFR : silica sol = 1 : 1; filler: *1*) marshallite, *2*) mullite, *3*) zircon).

presented in Fig. 3. For heat-treatment at 1050°C, the hot strength of the samples with no soaking, after soaking in a furnace for 5 h, and the strength after cooling to 20°C are indicated in the plot. After cooling, the strength of the samples dropped so much that they rapidly broke up during vibration. The fillers easily separated from the SiO_2 particles from the binder during vibration in water with surfactant or short-time milling in a ball mill. This made it possible to reuse fillers after the rod was extracted from the casting cavity.

As shown above, at the present time sintered rather than unsintered rods are preferred for casting critical parts. The sintering method was also used for pastes with CFR – silica sol binder. To avert a transition of silicon oxide from silica sol into cristobalite firing was conducted at temperature above 900°C. After cooling, the bending strength was 3 – 4 MPa. Permeation of CFR increased strength to 10 – 12 MPa. In Table 3 the properties of the new rods are compared with those of commercial rods. The new rods are

at least as good as the commercial rods in terms of their properties, but they were removed from the cast by means of not dissolution in aggressive media but rather vibration in water with a surfactant. After the rods were removed from the casting the fillers could be reused.

Attempts were made to use a polymorphic transition in Ca_2SiO_4 to weaken the rods. The transition from β-Ca_2SiO_4 into γ-Ca_2SiO_4 occurs below 400°C and is accompanied by a 10% volume increase. Since the rods possess adequate porosity and the amount of β-Ca_2SiO_4 is small, the pressing of a rod in the casting can be avoided and loss-of-strength can be realized. During heat treatment the β-Ca_2SiO_4 phase must be synthesized in the rod, as a result of which the rod would lose strength on cooling. The fillers must not cause β-Ca_2SiO_4 to vanish or stabilize. For example, mullite interacts with it and loss-of-strength does not occur. Weakening was observed when magnesium oxide, fused silicon oxide, corundum, and stabilized zirconium dioxide were used as fillers.

There are different ways to synthesize β-Ca_2SiO_4, for example, by using heat-hardened, thermoreactive polyorganic siloxane resin as a technological binder [6]. An amount of CaO appropriate to the reaction, so as to interact with active SiO_2, formed during break down of the resin, which leads to synthesis of β-Ca_2SiO_4 during sintering, was introduced into the paste. The strength of the unsintered blanks was 20 – 30 MPa and the hot strength at 1300°C was 18 – 24 MPa (USSR Inventor's Certificate No. 737097). Use of the binding properties of tricalcium silicate to form articles followed by synthesis of β-Ca_2SiO_4 holds a great deal of promise. The strength of the blanks was increased by permeation. To accelerate solidification of a blank in the mold krents (additives introduced into cement during milling in order to improve its properties) and rapid-setting binders (calcium and strontium aluminates) were used in the mold. Here the purity of the raw material and heat-treatment regimes play the most important role in order to avert stabilization of

TABLE 3. Comparison of the Strength of Commercially Produced and the New Rods

Property	Commercial rods		New rods, binder			
			Fused SiO_2, CFR		Marshallite, zircon, mullite, CFR – silica sol	
	unsintered	sintered	unsintered	sintered	unsintered	sintered
Bending strength, MPa:						
green part	3 – 4	7 – 35	20 – 25	7 – 8	7 – 8	10 – 14
at 300°C	1.5 – 2	7 – 35	3 – 4	7 – 8	1.5 – 2	3 – 4
at 1050°C after 5 h	7 – 8	5 – 25	20 – 23	20 – 25	8 – 10	8 – 10
at 1500°C after 1 h	7 – 9	0.5 – 1	25 – 30	25 – 30	10 – 12	10 – 12
at 20°C after cooling	7 – 8	14 – 50	0.5	0.5	0	0
Strength loss, %	–	–	97 – 99	100	97 – 99	100
Rod removal medium	NaOH		KHF_2		Surfactant	
Rod removal method	Etching				Vibration in water	

β-Ca_2SiO_4. Possible stabilizers and destabilizers of the $\beta - \gamma$ transition in Ca_2SiO_4 play are large role here [7].

CONCLUSIONS

In summary, methods developed for controlling polymorphic transitions in cristobalite and β-Ca_2SiO_4 in order to weaken ceramic materials were used to remove rods based on these materials from a metal casting with vibration in water containing surfactants without using aggressive and ecologically harmful reagents. Control of a polymorphic transition in cristobalite and β-Ca_2SiO_4 was used to weaken rods and then removing them from a casting by vibration in water containing a surfactant. The bending strength of cristobalite ceramic at 1050°C is about 20 MPa and that of β-Ca_2SiO_4 at 1300°C is 18 – 24 MPa, which is adequate to use these materials for rods. When quartz-glass powder was moistened with a solution containing sodium chloride as an additive the solution concentrated in active centers of the surface (self-organization), which served as seeds for converting glass into cristobalite. After cooling from 1050°C to room temperature the largest loss of strength in rods made from cristobalite synthesized from quartz glass was obtained by using a combined additive consisting of oxides (mass fraction, % in terms of SiO_2) taken in the ratio $Na_2O/MgO = 0.001/0.01$. In the sintering technology, quartz-glass rods were permeated with a CFR solution containing NaCl as a cristobalizing additive, where the CFR ensured that it would be uniformly distributed in the sample and that the strength of the sample would be high at room temperature. Owing to the polymorphism of cristobalite, the use of a mixture of CFR with silica sol for powders made from tridimite, mullite and zircon made it possible to finally attain weakening of the rods during cooling, the initial powers being easily removed during sieving from cristobalite and reused. In the sintering technology, rods based on CFR binder with silica sol were first sintered at 900°C, at which temperature there is still no cristobalite, and then successively permeated with oxalic acid and CFR and placed into the pattern paste. The weakening of the rods and their removal by vibration in water containing surfactants was implemented by polymorphic transformation from β-Ca_2SiO_4 into γ-Ca_2SiO_4 in pastes made from MgO, α-Al_2O_3, fused SiO_2 and stabilized ZrO_2; in addition, the rods were formed using a binder consisting of organosilicon resin with CaO additive or calcium silicate hydraulic binder, while β-Ca_2SiO_4 was synthesized in the process of heat-treatment of molds at 1050°C.

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